Chapter 8

8-1. The sample size is in the micro range and the analyte level is in the trace range. Hence, the analysis is a micro analysis of a trace constituent.

8-2. The objective of the sampling step is to produce a homogeneous laboratory sample of a few hundred grams or less having a composition that is identical to the average composition of the bulk of the material being sampled. Statistically, we try to obtain a mean value that is an unbiased estimate of the population mean and a variance that is an unbiased estimate of the population variance.

8-3. Step 1: Identify the population from which the sample is to be drawn.

Step 2: Collect the gross sample.

Step 3: Reduce the gross sample to a laboratory sample, which is a small quantity of homogeneous material

8-4. The gross sample mass is determined by (1) the uncertainty that can be tolerated between the composition of the gross sample and that of the whole, (2) the degree of heterogeneity of the whole, and (3) the level of particle size at which heterogeneity begins.

8-5. $s_o^2 = s_s^2 + s_m^2$

From the NIST sample: $s_m^2 = 0.00947$

From the gross sample: $s_o^2 = 0.15547$

$$s_s = \sqrt{0.15547 - 0.00947} = 0.38$$

The relative standard deviation = $\left(\frac{s_s}{\bar{x}}\right) \times 100\% = \left(\frac{0.38}{49.92}\right) \times 100\% = 0.76\%$

8-6. **(a)** $\sigma_r = \sqrt{(1-p)/Np}$ (where p = 14/250 = 0.0560)

$\sigma_r = \sqrt{(1-0.0560)/(250\times 0.0560)} = 0.260$ <u>or 26%</u>

(b) σ= 14 × 0.26 = 3.6 = <u>4 tablets</u>

95% CI = 14 ± $z\sigma\sqrt{N}$ = 14 ± 1.96 × 3.6 / $\sqrt{1}$ = 14 ± 7

(where z = 1.96 was obtained from Table 7-1)

(c) $N = (1 - 0.056)/[(0.05)^2 \times 0.056] = 6743 = 6.743 \times 10^3$

8-7. **(a)** $N = \dfrac{(1-p)}{p\sigma_r^2} = \dfrac{(1-0.02)}{0.02\,(0.20)^2} = \dfrac{49.0}{(0.20)^2} = 1225$

(b) $N = 49.0/(0.12)^2 = 3403$

(c) $N = 49.0/(0.07)^2 = 10000$

(d) $N = 49.0/(0.02)^2 = 122500$

8-8. **(a)** $250 = \dfrac{(1-52/250)}{(52/250)\times\sigma_r^2}$

$\sigma_r = 0.12 = 12\%$

(b) Here, the absolute standard deviation σof the estimate is sought.

σ = 750 × 12(52/250)0.12 = 224.6 = 220 broken bottles

(c) 90% CI = 750 × 12 × 52/250 ± $zs/\sqrt{N}$ = 1872 ± 1.64×224.6/$\sqrt{1}$

= 1872 ± 368 = 1900 ± 400 broken bottles

(d) $N = \dfrac{(1-0.21)}{0.21(0.05)^2} = 1500$ bottles

8-9. $N = p(1-p)\left(\dfrac{d_A d_B}{d^2}\right)^2\left(\dfrac{P_A - P_B}{\sigma_r P}\right)^2$

(a) $d = 7.3 \times 0.15 + 2.6 \times 0.85 = 3.3$

$P = 0.15 \times 7.3 \times 0.87 \times 100 / 3.3 = 29\%$

$N = 0.15(1-0.15)\left(\dfrac{7.3\times 2.6}{(3.3)^2}\right)^2\left(\dfrac{87-0}{0.020\times 29}\right)^2 = 8714$ particles

(b) mass $= (4/3)\pi(r)^3 \times d \times N = (4/3)\,\pi\,(0.175\text{ cm})^3 \times 3.3(\text{g/cm}^3) \times 8.714 \times 10^3$

$= 650$ g

(c) $0.500 = (4/3)\pi(r)^3 \times 3.3(\text{g/cm}^3) \times 8.714 \times 10^3$

$r = 0.016$ cm (diameter $= 0.32$ mm)

8-10. Recall that $s_o^2 = s_s^2 + s_m^2$. For both Scheme A and Scheme B the contribution of the method variance, s_m^2, will be both small relative to the sampling variance, s_s^2, and essentially the same. The sampling variancewill be lower for Scheme A, however, since 5 samples are blended and then evaluated as opposed to 3 samples that are unblended in Scheme B. Thus, Scheme A will have the lower variance.

8-11. (a) The following single-factor ANOVA table was generated using Excel's Data Analysis Tools:

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
1	3	185	61.66667	2.333333
2	3	172	57.33333	0.333333
3	3	146	48.66667	4.333333
4	3	170	56.66667	6.333333

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	264.25	3	88.08333	26.425	0.000167	4.066181
Within Groups	26.66667	8	3.333333			
Total	290.9167	11				

The Between Groups *SS* value of 264.25 compared to the Within Groups value of 26.66667 indicates that the mean concentrations vary significantly from day to day.

(b) SST is the total variance and is the sum of the within day variance, SSE, and the day-to-day variance, SSF; SST = SSE + SSF. The within day variance, SSE, reflects the method variance, SSM. The day-to-day variance, SSF, reflects the sum of the method variance, SSM, and the sampling variance, SSS; SSF = SSM + SSS. Thus,

SST = SSM + SSM + SSS and SSS = SST – 2×SSM

SSS = 290.92 – 2×26.67 = 237.58. Dividing 3 degrees of freedom gives a mean square (estimates sampling variance σ_s^2) of 79.19.

(c) The best approach to lowering the overall variance would be to reduce the sampling variance, since this is the major component of the total variance (σ_t^2 = 88.08333).

8-12. See Example 8-1

$d = 7.3 \times 0.01 + 2.6 \times 0.99 = 2.6 \text{ g/cm}^3$

$P = 0.01 \times 7.3 \times 0.87 \times 100 / 2.6 = 2.4\%$

$$N = 0.01(1 - 0.01)\left(\frac{7.3 \times 2.6}{2.6 \times 2.6}\right)^2\left(\frac{87 - 0}{0.05 \times 2.4}\right)^2 = 4.1 \times 10^4 \text{ particles}$$

mass $= (4/3)\pi(0.25)^3 \times 2.6 \times 4.1 \times 10^4 / 454 = 15$ lb;

Since the seller took only a 5 lb sample and 15 lbs was needed, this is insufficient.

8-13. See Example 8-3

Using $t = 1.96$ for infinite samples $N = \frac{(1.96)^2 \times (0.3)^2}{(3.7)^2 \times (0.07)^2} = 5.16$

Using $t = 2.78$ for 5 samples (4 df) $N = \frac{(2.78)^2 \times (0.3)^2}{(3.7)^2 \times (0.07)^2} = 10.36$

Using $t = 2.26$ for 10 samples $N = \frac{(2.26)^2 \times (0.3)^2}{(3.7)^2 \times (0.07)^2} = 6.85$

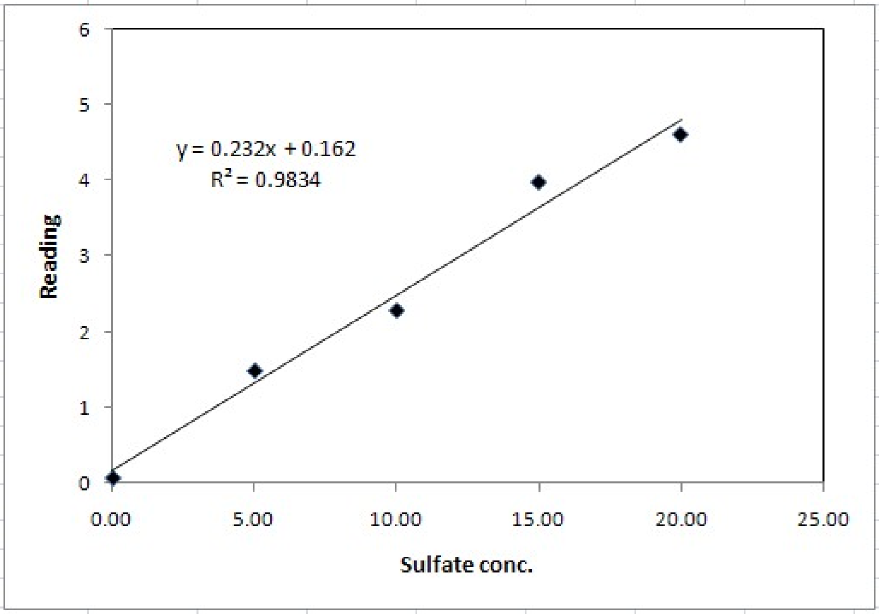
Using $t = 2.45$ for 7 samples $N = \frac{(2.45)^2 \times (0.3)^2}{(3.7)^2 \times (0.07)^2} = 8.05$

Using $t = 2.36$ for 8 samples $N = \frac{(2.36)^2 \times (0.3)^2}{(3.7)^2 \times (0.07)^2} = 7.47$

The iterations converge at between 7 and 8 samples, so 8 should be taken for safety.

8-14.

	A	B
1	**Pb 8-14**	
2	C_x	Reading
3	0.00	0.06
4	5.00	1.48
5	10.00	2.28
6	15.0	3.98
7	20.0	4.61
8	Unknown	2.84
9	**Part (b)**	
10	Slope	0.232
11	Intercept	0.162
12	Std. Error	0.275245
13	*N*	5
14	S_{xx}	250
15	ybar	2.482
16	**Part (e)**	
17	*M*	1
18	$c_{unknown}$	11.5431
19	SD in *c*	1.304786
20	CV	11.3036
21	**Part (f)**	
22	*M*	6
23	$c_{unknown}$	11.5431
24	SD in *c*	0.727673
25	CV	6.303965
26		
27	**Spreadsheet Documentation**	
28	B10=SLOPE(B3:B7,A3:A7)	
29	B11=INTERCEPT(B3:B7,A3:A7)	
30	B12=STEYX(B3:B7,A3:A7)	
31	B13=COUNT(A3:A7)	
32	B14=DEVSQ(A3:A7)	
33	B15=AVERAGE(B3:B7)	
34	B18=(B8-B11)/B10	
35	B19=(B12/B10)*SQRT(1/B17+1/B13+((B8-B15)^2)/((B10^2)*B14))	
36	B20=B19/B18*100	
37	B22=(B8-B11)/B10	
38	B23=(B12/B10)*SQRT(1/B22+1/B13+((B8-B15)^2)/((B10^2)*B14))	
39	B24=B24/B18*100	



(a) See spreadsheet

(b) m = 0.232 and b = 0.162

(c) See spreadsheet

(d) Regression statistic generated using Excel's Data Analysis Tools

	A	B	C	D	E	F	G	H	I
1	SUMMARY OUTPUT								
2									
3	*Regression Statistics*								
4	Multiple R	0.991660198							
5	R Square	0.983389947							
6	Adjusted R Square	0.977853263							
7	Standard Error	0.275245345							
8	Observations	5							
9									
10	ANOVA								
11		*df*	*SS*	*MS*	*F*	*Significance F*			
12	Regression	1	13.456	13.456	177.6135	0.000913111			
13	Residual	3	0.22728	0.07576					
14	Total	4	13.68328						
15									
16		*Coefficients*	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
17	Intercept	0.162	0.213204128	0.759835	0.502609	-0.51651069	0.840511	-0.51651069	0.84051069
18	X Variable 1	0.232	0.017408044	13.32717	0.000913	0.176599834	0.2874	0.17659983	0.28740017
19									

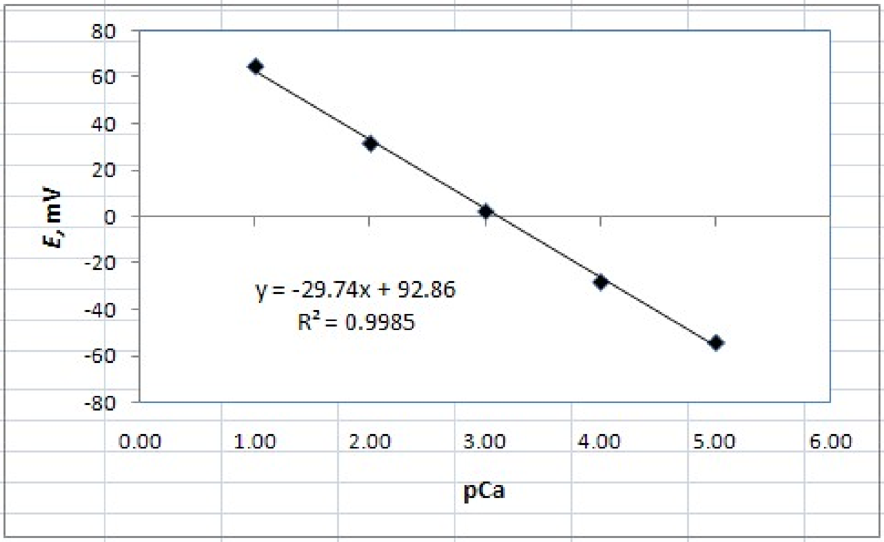
The large F value of 177.6 indicates that the regression is significant. The R^2 value of 0.9834 measures the fraction of the variation explained by the regression. The adjusted R^2 value of 0.9779 indicates the price to pay for adding an additional parameter.

(e) c_{Unk} = 11.5 mg/mL; s_{Unk} = 1.3 mg/mL; CV = 11.3%

(f) c_{Unk} = 11.5 mg/mL; s_{Unk} = 0.73 mg/mL; CV = 6.3%

8-15.

	A	B
1	**Pb 8-15**	
2	pCa	E, mV
3	5.00	-53.8
4	4.00	-27.7
5	3.00	2.7
6	2.00	31.9
7	1.00	65.1
8	unknown	15.3
9	**Part (b)**	
10	Slope	-29.74
11	Intercept	92.86
12	Std. Error	2.138224
13	*N*	5
14	S_{xx}	10
15	*y* bar	3.64
16	**Part (d)**	
17	*M*	1
18	pCa unknwn	2.607935
19	SD in pCa	0.079262
20	RSD	0.030393
21	**Part(e)**	
22	*M*	2
23	SD in pCa	0.06081
24	RSD	0.023317
25	*M*	8
26	SD in pCa	0.041946
27	RSD	0.016084
28	**Spreadsheet Documentation**	
29	B10=SLOPE(B3:B7,A3:A7)	
30	B11=INTERCEPT(B3:B7,A3:A7)	
31	B12=STEYX(B3:B7,A3:A7)	
32	B13=COUNT(A3:A7)	
33	B14=DEVSQ(A3:A7)	
34	B15=AVERAGE(B3:B7)	
35	B18=(B8-B11)/B10	
36	B19=ABS((B12/B10)*SQRT(1/B17+1/B13+((B8-B15)^2)/((B10^2)*B14)))	
37	B20=B19/B18	
38	B23=ABS((B12/B10)*SQRT(1/B22+1/B13+((B8-B15)^2)/((B10^2)*B14)))	
39	B24=B23/B18	
40	B26=ABS((B12/B10)*SQRT(1/B25+1/B13+((B8-B15)^2)/((B10^2)*B14)))	
41	B27=B26/B18	



(a) See spreadsheet

(b) Equation of the line: y = –29.74 x + 92.86

(c) Regression statistics generated with Excel's Data Analysis Tools

	A	B	C	D	E	F	G	H	I
1	SUMMARY OUTPUT								
2									
3	*Regression Statistics*								
4	Multiple R	0.999225519							
5	R Square	0.998451638							
6	Adjusted R Square	0.997935517							
7	Standard Error	2.138223562							
8	Observations	5							
9									
10	ANOVA								
11		*df*	*SS*	*MS*	*F*	*Significance F*			
12	Regression	1	8844.676	8844.676	1934.531	2.58702E-05			
13	Residual	3	13.716	4.572					
14	Total	4	8858.392						
15									
16		*Coefficients*	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
17	Intercept	92.86	2.242587791	41.40752	3.1E-05	85.72308477	99.99692	85.72308477	99.9969152
18	X Variable 1	-29.74	0.67616566	-43.9833	2.59E-05	-31.89186091	-27.5881	-31.8918609	-27.588139

The large F value of 1934.5 indicates that the regression is significant. The R^2 value of 0.9985 measures the fraction of the variation explained by the regression. The adjusted R^2 value of 0.9979 indicates the price to pay for adding an additional parameter.

(d) pCa_{Unk} = 2.608; SD in pCa = 0.079; RSD = 0.030 (CV = 3.0%)

(e) For 2 replicate measurements:

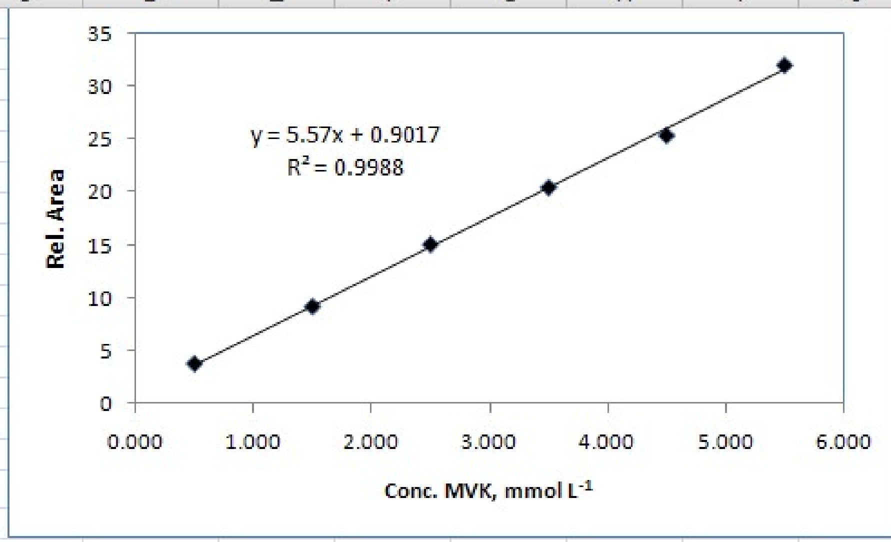
pCa_{Unk} = 2.608; SD in pCa = 0.061; RSD = 0.023 (CV = 2.3%)

For 8 replicate measurements:

pCa_{Unk} = 2.608; SD in pCa = 0.042: RSD = 0.016 (CV = 1.6%)

8-16.

	A	B	C	D	E	F	G	H	I	J
1	**Pb8-16**									
2	Conc. MVK	Rel. Area								
3	0.500	3.76								
4	1.50	9.16								
5	2.50	15.03								
6	3.50	20.42								
7	4.50	25.33								
8	5.50	31.97								
9	unknown1	12.9								
10	unknown2	21.3								
11	**Part (a)**									
12	Slope	5.57								
13	Intercept	0.901667								
14	Std. Error	0.40303								
15	*N*	6								
16	S_{xx}	17.5								
17	ybar	17.61167								
18	**Parts (d)-(f)**									
19	*M*	1		*M*	4					
20	*c* unk 1	2.154099		*c* unk 1	2.154099					
21	SD unk 1	0.079513		SD unk 1	0.048945					
22	RSD unk 1	0.036912		RSD unk 1	0.022722					
23	*c* unk 2	3.662178		*c* unk 2	3.662178					
24	SD unk 2	0.07899		SD unk 2	0.04809					
25	RSD unk 2	0.021569		RSD unk 2	0.013132					
26	**Spreadsheet Documentation**									
27	B12=SLOPE(B3:B8,A3:A8)									
28	B13=INTERCEPT(B3:B8,A3:A8)									
29	B14=STEYX(B3:B8,A3:A8)									
30	B15=COUNT(A3:A8)									
31	B16=DEVSQ(A3:A8)									
32	B17=AVERAGE(B3:B8)									
33	B20=(B9-B13)/B12									
34	B21=(B14/B12)*SQRT(1/B19+1/B15+((B9-B17)^2)/((B12^2)*B16))									
35	B22=B21/B20									
36	E20=(B9-B13)/B12									
37	E21=(B14/B12)*SQRT(1/E19+1/B15+((B9-B17)^2)/((B12^2)*B16))									
38	E22=E21/E20									



(a) m = 5.57 and b = 0.90

(b) Regression statistics

	A	B	C	D	E	F	G	H	I
1	SUMMARY OUTPUT								
2									
3	*Regression Statistics*								
4	Multiple R	0.999402185							
5	R Square	0.998804726							
6	Adjusted R Square	0.998505908							
7	Standard Error	0.403030189							
8	Observations	6							
9									
10	ANOVA								
11		*df*	*SS*	*MS*	*F*	*Significance F*			
12	Regression	1	542.93575	542.9358	3342.514	5.35968E-07			
13	Residual	4	0.649733333	0.162433					
14	Total	5	543.5854833						
15									
16		*Coefficients*	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
17	Intercept	0.901666667	0.332579863	2.711128	0.053475	-0.021723065	1.825056	-0.02172307	1.825056399
18	X Variable 1	5.57	0.096342642	57.81448	5.36E-07	5.302509942	5.83749	5.302509942	5.837490058
19									

(c) See spreadsheet

(d) *c* of MVK in unknown 1 = 2.15 mmol L^{-1}

(e) For 1 measurement, SD = 0.080 mmol L^{-1}; RSD = 0.037

For 4 replicates, SD = 0.049 mmol L^{-1}; RSD = 0.023

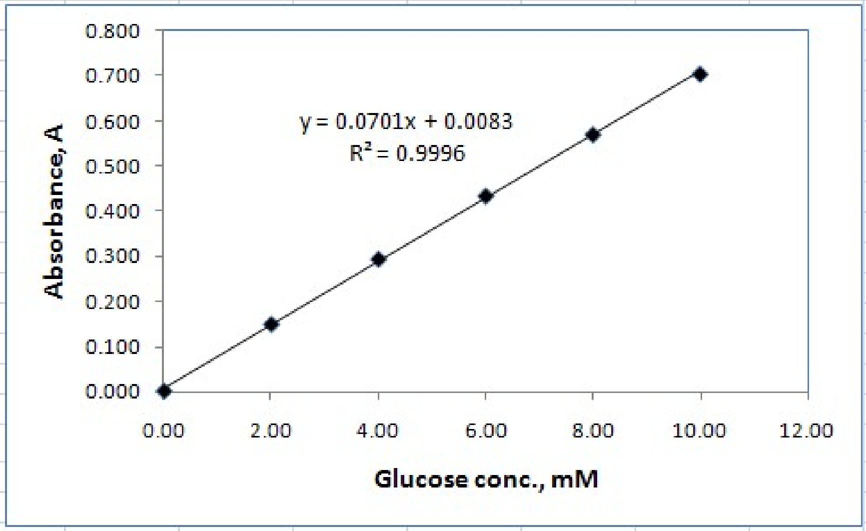
(f) *c* of MVK in unknown 2 = 3.66 mmol L^{-1}

SD for 1 measurement = 0.079; RSD = 0.022

SD for 4 replicates = 0.048; RSD = 0.013

8-17.

	A	B	C	D	E	F	G
1	**Pb 8-17**						
2	Glucose conc.	Absorbance					
3	0.00	0.002					
4	2.00	0.150					
5	4.00	0.294					
6	6.00	0.434					
7	8.00	0.570					
8	10.00	0.704					
9	unknown	0.413					
10	**Part (a)**						
11	Slope	0.070143					
12	Intercept	0.008286					
13	Std. Error	0.005581					
14	*N*	6					
15	S_{xx}	70					
16	*y* bar	0.359					
17	**Parts (b) & (c)**						
18	SD *m*	0.000667					
19	SD *b*	0.004039		**LINEST Results**			
20	*t*(0.05,4)	2.776445		*m*	0.070143	0.008286	*b*
21	95% CI for *m*	0.001852		SD *m*	0.000667	0.004039	SD *b*
22	95% CI for *b*	0.011214		R^2	0.999638	0.005581	SE
23	**Part (d)**			*F*	11058.76	4	df
24	*M*	1		SSR	0.344401	0.000125	SSE
25	c_{unk}	5.769857					
26	SD in c_{unk}	0.086246					
27	95% CI for c_{unk}	0.239458					
28	**Spreadsheet Documentation**						
29	B11=SLOPE(B3:B8,A3:A8)			E20:F24=LINEST(B3:B8,A3:A8,,TRUE)			
30	B12=INTERCEPT(B3:B8,A3:A8)			B20=TINV(0.05,4)			
31	B13=STEYX(B3:B8,A3:A8)			B21=B20*B18			
32	B14=COUNT(A3:A8)			B22=B20*B19			
33	B15=DEVSQ(A3:A8)			B25=(B9-B12)/B11			
34	B16=AVERAGE(B3:B8)			B26=(B13/B11)*SQRT(1/B24+1/B14+((B9-B16)^2)/((B11^2)*B15))			
35	B18=E21			B27=B20*B26			
36	B19=F21						



(a) $m = 0.07014$ and $b = 0.008286$

(b) $s_m = 0.00067$; $s_b = 0.004039$; SE = 0.00558

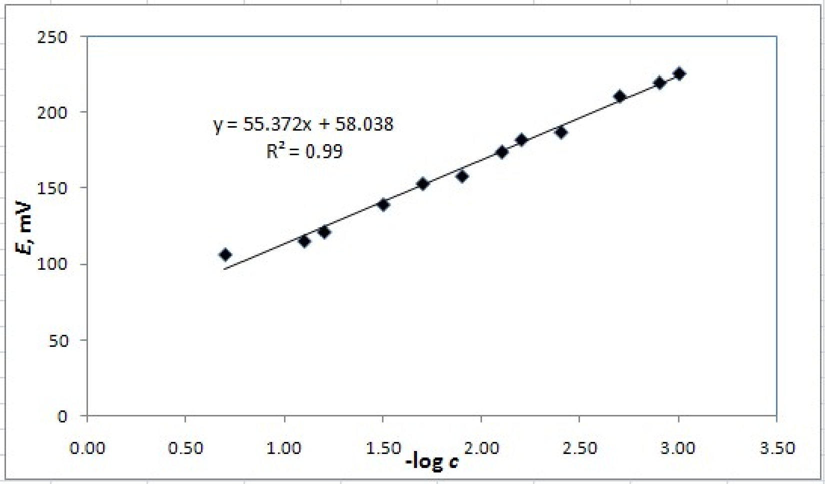
(c) 95% $CI_m = m \pm t \times s_m = 0.07014 \pm 0.0019$

95% $CI_b = b \pm t \times s_b = 0.0083 \pm 0.0112$

(d) $c_{unk} = 5.77$ mM; $s_{unk} = 0.09$; 95% $CI_{unk} = c_{unk} \pm t \times s_{Unk} = 5.77 \pm 0.24$ mM

8-18.

	A	B	C	D
1	**Pb 8-18**			
2	**Part (a)**			
3	*c*, M	-log *c*	*E*, mV	
4	0.20000	0.69897	106	
5	0.07940	1.10018	115	
6	0.06310	1.19997	121	
7	0.03160	1.50031	139	
8	0.02000	1.69897	153	
9	0.01260	1.89963	158	
10	0.00794	2.10018	174	
11	0.00631	2.19997	182	
12	0.00398	2.40012	187	
13	0.00200	2.69897	211	
14	0.00126	2.89963	220	
15	0.00100	3.00000	226	
16	**Part (b)**			
17	Slope	55.37223		
18	Intercept	58.03846		
19	**Part (c)**			
20	**LINEST Values**			
21	*m*	55.37223	58.03846	*b*
22	SD *m*	1.755512	3.639897	SD *b*
23	R^2	0.990049	4.289517	SE
24	*F*	994.8936	10	df
25	SSR	18306	183.9996	SSE
26				
27	*t*(0.05,10)	2.228139		
28	95% CI for *m*	3.911523		
29	95% CI for *b*	8.110195		
30	**Spreadsheet Documentation**			
31	B4=-LOG(A4)			
32	B17=SLOPE(C4:C15,B4:B15)			
33	B18=INTERCEPT(C4:C15,B4:B15)			
34	B21:C25=LINEST(C4:C15,B4:B15,,TRUE)			
35	B27=TINV(0.05,10)			
36	B28=B27*B22			
37	B29=B27*C22			



(a). See spreadsheet

(b). ***m* = 55.37; *b* = 58.04;** $y = 55.37\,x + 58.04$

(c). 95% CI_m = 55.37 ± 3.91 and 95% CI_b = 58.04 ± 8.11

(d). From the LINEST values, $F = 994.9$. This large value indicates that the regression is significant.

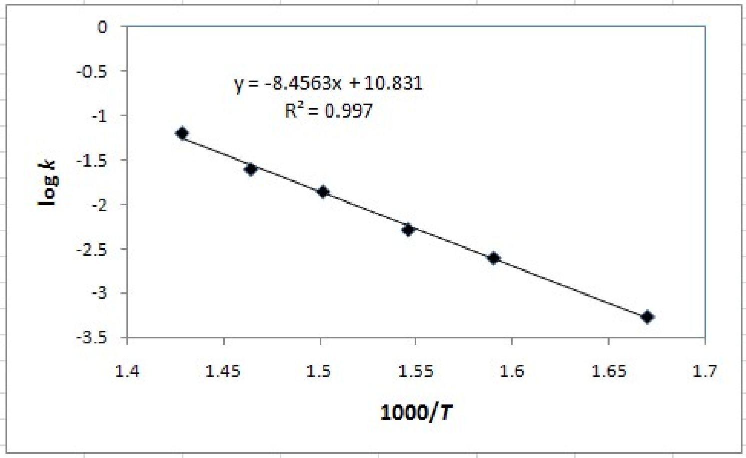
(e). Regression statistics via Excel's Data Analysis Tools:

	A	B	C	D	E	F	G	H	I
1	SUMMARY OUTPUT								
2									
3	*Regression Statistics*								
4	Multiple R	0.995011908							
5	R Square	0.990048698							
6	Adjusted R Square	0.989053568							
7	Standard Error	4.289517151							
8	Observations	12							
9									
10	ANOVA								
11		*df*	*SS*	*MS*	*F*	*Significance F*			
12	Regression	1	18306.00043	18306	994.8936	2.41162E-11			
13	Residual	10	183.9995739	18.39996					
14	Total	11	18490						
15									
16		*Coefficients*	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
17	Intercept	58.03845931	3.639896675	15.94508	1.94E-08	49.92826415	66.14865	49.9282641	66.14865447
18	X Variable 1	55.37223056	1.755511558	31.54193	2.41E-11	51.46070707	59.28375	51.4607071	59.28375405
19									

From either LINEST or the regression statistics, the standard error = 4.29. The correlation coefficient $R = \sqrt{R^2} = \sqrt{0.990048698} = 0.995$, and the multiple R is also 0.995.

8-19.

	A	B	C	D
1	**Pb 8-19**			
2	**Part (a)**			
3	*T*, K	*k*, s^{-1}	1000/*T*	log *k*
4	599	0.00054	1.669449	-3.26761
5	629	0.0025	1.589825	-2.60206
6	647	0.0052	1.545595	-2.284
7	666	0.014	1.501502	-1.85387
8	683	0.025	1.464129	-1.60206
9	700	0.064	1.428571	-1.19382
10	**Part (b)**			
11	Slope	-8.45629		
12	Intercept	10.8311		
13	Std. Error	0.045927		
14	*N*	6		
15	S_{xx}	0.038647		
16	*y*bar	-2.1339		
17	**Part (c)**			
18	**LINEST values**			
19	*m*	-8.45629	10.8311	*b*
20	SD in *m*	0.23362	0.358671	SD in *b*
21	R^2	0.996956	0.045927	SE
22	*F*	1310.21	4	df
23	SSR	2.763575	0.008437	SSE
24	E_A	38696.51		
25	SD in E_A	1069.058		
26	**Spreadsheet Documentation**			
27	C4=1000/A4			
28	D4=LOG(B4)			
29	B11=SLOPE(D4:D9,C4:C9)			
30	B12=INTERCEPT(D4:D9,C4:C9)			
31	B13=STEYX(D4:D9,C4:C9)			
32	B14=COUNT(C4:C9)			
33	B15=DEVSQ(C4:C9)			
34	B16=AVERAGE(D4:D9)			
35	B19:C23=LINEST(D4:D9,C4:C9,,TRUE)			
36	B24=-B11*2.303*1.987*1000			
37	B25=B20*2.303*1.987*1000			



(a) See Spreadsheet

(b) $m = -8.456$; $b = 10.83$ and SE = 0.0459

(c) $E_A = -m \times 2.303 \times R \times 1000$ (Note: m has units of mK) =

$-(-8.456\text{ mK})\times(2.303)\times(1.987\text{ cal mol}^{-1}\text{ K}^{-1})\times(1000\text{ K/mK})$

$= 38697$ cal/mol

$s_{EA} = s_m \times 2.303 \times R \times 1000$

$= 1069$ cal/mol

Thus, E_A = 38,697 ± 1069 cal/mol or 38.7 ± 1.1 kcal/mol

(d) H_0: E_A = 41.00 kcal/mol; H_A: $E_A \neq$ 41.00 kcal/mol.

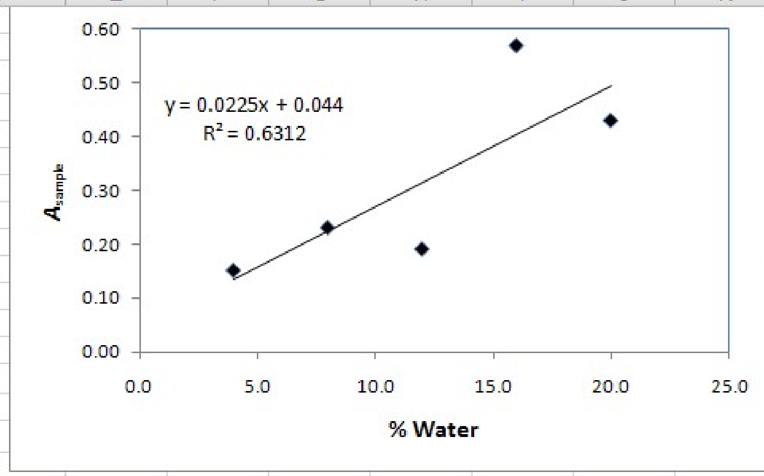
$t = (38.697 - 41.00)/1.069 = -2.15$

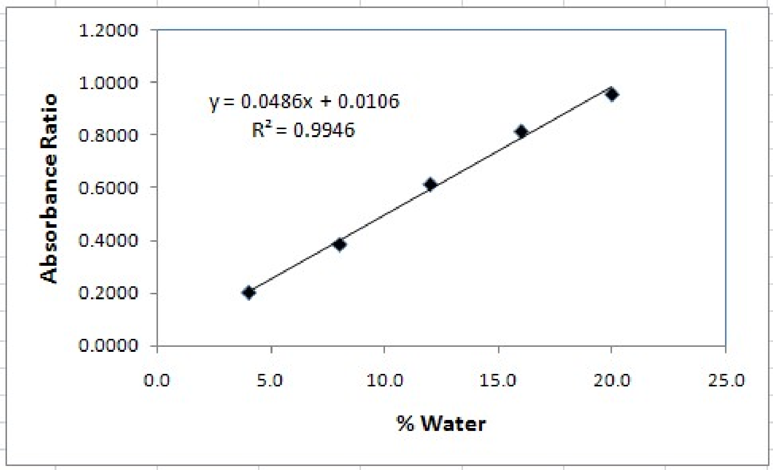
$t(0.025, 4) = 2.776$

Since $t > -t_{crit}$ we retain H_0. There is no reason to doubt that E_A is not 41.00 kcal/mol at the 95% confidence level.

8-20.

	A	B	C	D
1	**Pb 8-20**			
2	**Part (a)**			
3	% Water	A_{sample}	A_{std}	
4	4.0	0.15	0.75	
5	8.0	0.23	0.60	
6	12.0	0.19	0.31	
7	16.0	0.57	0.70	
8	20.0	0.43	0.45	
9	unknown	0.37	0.47	
10				
11	**LINEST values**			
12	*m*	0.0225	0.044	*b*
13	SD *m*	0.009929	0.131722	SD *b*
14	R^2	0.631234	0.125592	SE
15	*F*	5.135249	3	df
16	SSR	0.081	0.04732	SSE
17				
18	**Part (b)**			
19	% Water	*A* ratio		
20	4.0	0.2000		
21	8.0	0.3833		
22	12.0	0.6129		
23	16.0	0.8143		
24	20.0	0.9556		
25	unknown	0.7872		
26				
27	**LINEST values**			
28	*m*	0.048552	0.010597	*b*
29	SD *m*	0.002071	0.027469	SD *b*
30	R^2	0.994573	0.026191	SE
31	*F*	549.8363	3	df
32	SSR	0.377161	0.002058	SSE
33				
34	**Part (c)**			
35	% Water, unk.	15.99613		
36				
37	**Spreadsheet Documentation**			
38	B12:C16=LINEST(B4:B8,A4:A8,,TRUE)			
39	B20=B4/C4			
40	B28:C32=LINEST(B20:B24,A20:A24,,TRUE)			
41	B35=(B25-C28)/B28			





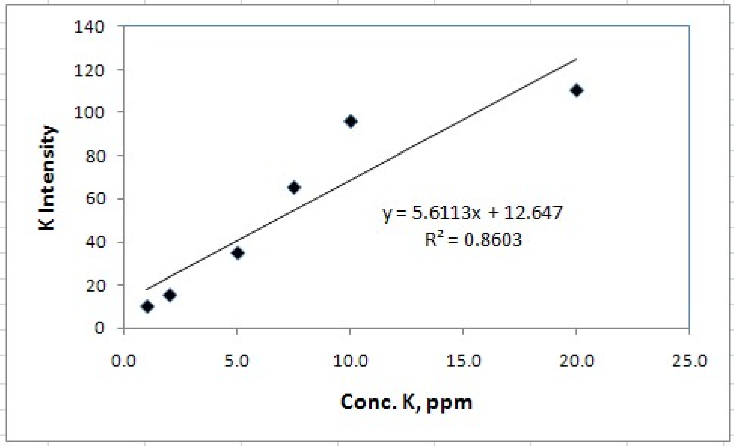
(a) See Spreadsheet

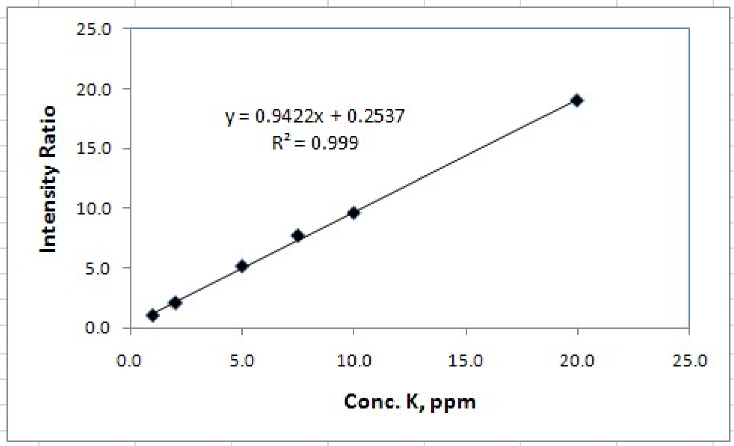
(b) The linearity is much better when using internal standards (compare R^2 and *F* values). Taking the ratio compensates for systematic errors that affect both the sample and the internal standard.

(c) 15.996% rounded to 16.0%

8-21.

	A	B	C	D
1	**Pb 8-21**			
2	**Part (a)**			
3	Conc. K, ppm	Int. K	Int. Li	
4	1.0	10	10	
5	2.0	15.3	7.5	
6	5.0	34.7	6.8	
7	7.5	65.2	8.5	
8	10.0	95.8	10	
9	20.0	110.2	5.8	
10	unknown	47.3	9.1	
11				
12	**LINEST values**			
13	*m*	5.611332	12.6474	*b*
14	SD *m*	1.130792	11.1776	SD *b*
15	R^2	0.860259	17.56219	SE
16	*F*	24.62446	4	df
17	SSR	7594.938	1233.722	SSE
18				
19	**Part (b)**			
20	Conc. K, ppm	Int. Ratio		
21	1.0	1.000		
22	2.0	2.040		
23	5.0	5.103		
24	7.5	7.671		
25	10.0	9.580		
26	20.0	19.000		
27	unknown	5.198		
28				
29	**LINEST values**			
30	*m*	0.942228	0.253694	*b*
31	SD *m*	0.014703	0.145339	SD *b*
32	R^2	0.999027	0.228356	SE
33	*F*	4106.561	4	df
34	SSR	214.1431	0.208586	SSE
35				
36	Conc. K unk.	5.247253		
37				
38	**Spreadsheet Documentation**			
39	B13:C17=LINEST(B4:B9,A4:A9,,TRUE)			
40	B21=B4/C4			
41	B30:C34=LINEST(B21:B26,A21:A26,,TRUE)			
42	B36=(B27-C30)/B30			





(a) See Spreadsheet

(b) The linearity is much better when using internal standards (compare R^2 and *F* values). Taking the ratio compensates for systematic errors that affect both the sample and the internal standard.

(c) 5.247 ppm rounded to 5.2 ppm

8-22. **(a)**

$$\frac{c_{\text{Unk}}}{(V_{\text{Std}}c_{\text{Std}}+V_{\text{Unk}}c_{\text{Unk}})/V_{\text{Tot}}}=\frac{A(\text{sample - blank})}{A(\text{sample} + \text{addition - blank})}$$

$$\frac{c_{\text{Unk}}}{\dfrac{(0.1000\text{ mL}\times 1000\ \mu\text{g/mL}+100.0\text{ mL}\times c_{\text{Unk}})}{(100.1\text{ mL})}}=\frac{(0.520-0.020)}{1.020}$$

$$\frac{c_{\text{Unk}}}{0.99900+0.99900c_{\text{Unk}}} = 0.490196$$

c_{Unk} = 0.490196(0.99900 + 0.99900 c_{Unk})

0.510294 c_{Unk} = 0.489706

c_{Unk} = 0.96 μg/mL

(b)

$$\frac{c_{\text{Unk}}}{\dfrac{(0.1000\text{ mL}\times 1000\ \mu\text{g/mL}+100.0\text{ mL}\times c_{\text{Unk}})}{(100.1\text{ mL})}}=\frac{(0.520-0.100)}{(1.020-0.080)}$$

Proceeding as in (a) we obtain c_{Unk} = 0.81 μg/mL

%error = (0.96 – 0.81)/0.81 × 100% = 19%

8-23. See Example 8-8

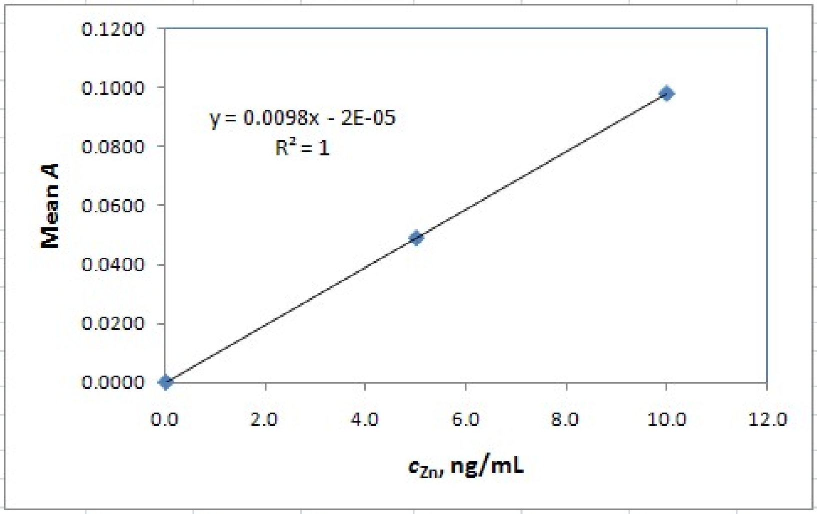
$$c_{\text{u}} = \frac{(0.300)(1.00\times 10^{-3})(1.00)}{(0.530)(51.00)-(0.300)(50.00)} = 2.4938\times 10^{-5}\text{ M}$$

To obtain the concentration of the original sample, we need to multiply by 25.00/1.00.

c_{u} = $(2.4938\times10^{-5}$ M)(25.00)/(1.00) = 6.23×10^{-4} M

8-24.

	A	B	C	D	E	F
1	**Pb 8-22**					
2	**Part (a)**					
3	c_{Zn}, ng/mL	*A*	*A*	*A*	Mean	SD
4	0.0				0.0000	0.0047
5	5.0	0.0519	0.0463	0.0485	0.04890	0.002821
6	10.0	0.0980	0.1033	0.0925	0.09793	0.005400
7	Sample	0.0672	0.0614	0.0661	0.06490	0.003081
8	**Part (b)**					
9	Slope	0.009793333				
10	Intercept	-2.22222E-05				
11	Std. Error	5.44331E-05				
12	*N*	3				
13	S_{xx}	50				
14	*y* bar	0.0489				
15	Calibration sensit.	0.009793333				
16	Anal. sensit.	3.471154967				
17	**Part (c)**					
18	DL = $k s_{bk}$/m	1.439754935				
19	**Part (d)**					
20	c_{unk}	6.629226231				
21	*M*	3				
22	SD in c_{unk}	0.004715467				
23	**Spreadsheet Documentation**					
24	E5=AVERAGE(B5:D5)					
25	F5=STDEV(B5:D5)					
26	B9=SLOPE(E4:E6,A4:A6)					
27	B10=INTERCEPT(E4:E6,A4:A6)					
28	B11=STEYX(E4:E6,A4:A6)					
29	B12=COUNT(A4:A6)					
30	B13=DEVSQ(A4:A6)					
31	B14=AVERAGE(E4:E6)					
32	B15=B9					
33	B16=B9/F5					
34	B18=3*F4/B9					
35	B20=(E7-B10)/B9					
36	B22=(B11/B9)*SQRT(1/B21+1/B12+((E7-B14)^2)/((B9^2)*B13))					



(a) See Spreadsheet

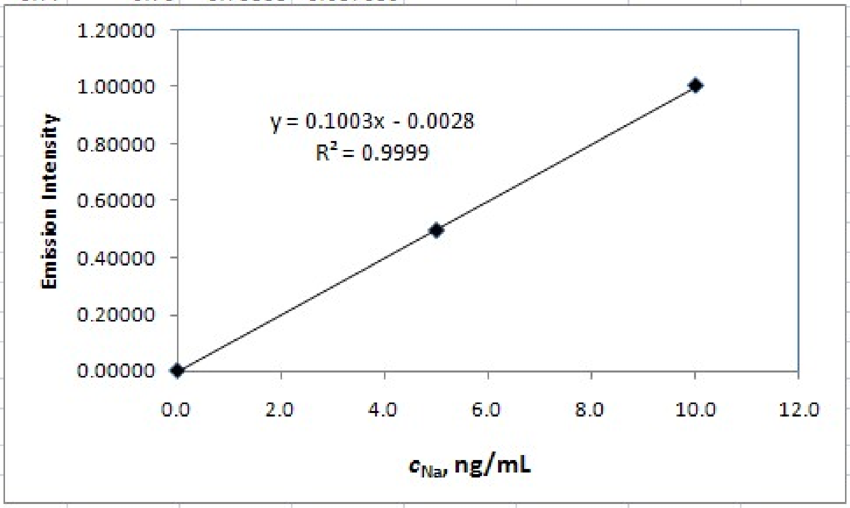
(b) calibration sensitivity = 0.0098; analytical sensitivity = 3.47

(c) For k = 3, DL = 1.44 ng/mL. This is a confidence level of 98.3%.

(d) c_{Zn} = 6.629 ± 0.005 ng/mL

8-25.

	A	B	C	D	E	F	G	H	I	J
1	**Pb 8-25**									
2	**Part (a)**									
3	c_{Na}, ng/mL		Emission Intensity		Mean	SD				
4	0.0				0.00000	0.0071				
5	5.0	0.51	0.49	0.48	0.49333	0.015275				
6	10.0	1.02	1.00	0.99	1.00333	0.015275				
7	Sample	0.71	0.77	0.78	0.75333	0.037859				
8	**Part (b)**									
9	Slope	0.100333								
10	Intercept	-0.00278								
11	Std. Error	0.006804								
12	*N*	3								
13	S_{xx}	50								
14	*y* bar	0.4989								
15	Calibration sensit.	0.100333								
16	Anal. sensit.	6.568358								
17	**Part (c)**									
18	*k*	2								
19	DL = $k s_{bk}$/m	0.141528								
20	*k*	3								
21	DL = $k s_{bk}$/m	0.212292								
22	**Part (d)**									
23	c_{unk}	7.535991								
24	*M*	3								
25	SD in c_{unk}	0.060477								
26	**Spreadsheet Documentation**									
27	E5=AVERAGE(B5:D5)									
28	F5=STDEV(B5:D5)									
29	B9=SLOPE(E4:E6,A4:A6)									
30	B10=INTERCEPT(E4:E6,A4:A6)									
31	B11=INTERCEPT(E4:E6,A4:A6)									
32	B12=COUNT(A4:A6)									
33	B13=DEVSQ(A4:A6)									
34	B14=AVERAGE(E4:E6)									
35	B15=B9									
36	B16=B9/F5									
37	B19=B18*F4/B9									
38	B21=B20*F4/B9									
39	B23=(E7-B10)/B9									
40	B25=(B11/B9)*SQRT(1/B24+1/B12+((E7-B14)^2)/((B9^2)*B13))									



(a) See Spreadsheet

(b) calibration sensitivity = 0.100; analytical sensitivity = 6.57

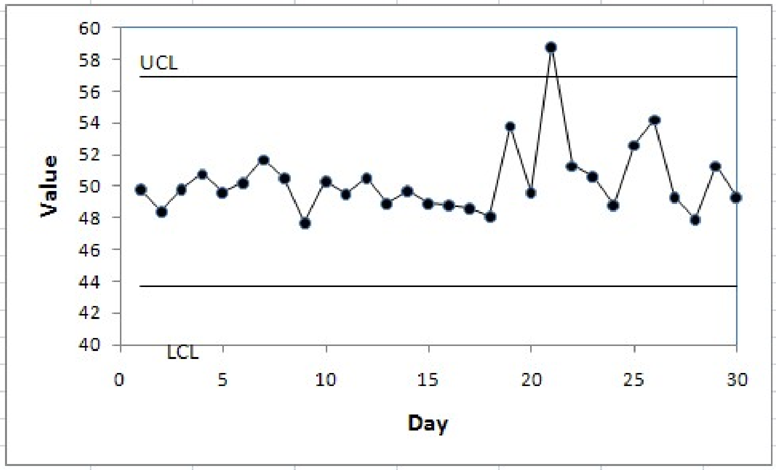
(c) For k = 2, DL = 0.14 ng/mL (92.1% confidence level)

for k = 3, DL = 0.21 ng/mL (98.3% confidence level)

(d) c_{Na} = 7.54 ± 0.06 ng/mL

8-26.

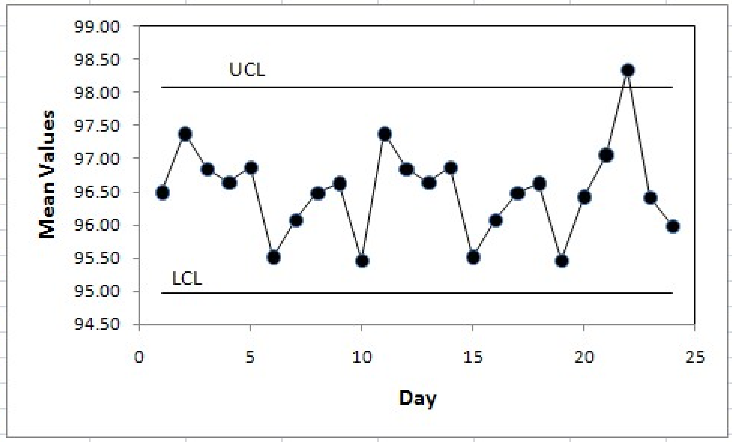
	A	B	C	D	E	F	G	H
1	**Pb 8-26**							
2	Day	Value	UCL	LCL				
3	1	49.8	56.9	43.7				
4	2	48.4	56.9	43.7				
5	3	49.8	56.9	43.7				
6	4	50.8	56.9	43.7				
7	5	49.6	56.9	43.7				
8	6	50.2	56.9	43.7				
9	7	51.7	56.9	43.7				
10	8	50.5	56.9	43.7				
11	9	47.7	56.9	43.7				
12	10	50.3	56.9	43.7				
13	11	49.5	56.9	43.7				
14	12	50.5	56.9	43.7				
15	13	48.9	56.9	43.7				
16	14	49.7	56.9	43.7				
17	15	48.9	56.9	43.7				
18	16	48.8	56.9	43.7				
19	17	48.6	56.9	43.7				
20	18	48.1	56.9	43.7				
21	19	53.8	56.9	43.7				
22	20	49.6	56.9	43.7				
23	21	58.8	56.9	43.7				
24	22	51.3	56.9	43.7				
25	23	50.6	56.9	43.7				
26	24	48.8	56.9	43.7				
27	25	52.6	56.9	43.7				
28	26	54.2	56.9	43.7				
29	27	49.3	56.9	43.7				
30	28	47.9	56.9	43.7				
31	29	51.3	56.9	43.7				
32	30	49.3	56.9	43.7				
33	Mean	50.31			**Spreadsheet Documentation**			
34	Sigma	2.207163			B33=AVERAGE(B3:B32)			C3=$B$35
35	UCL	56.93149			B34=STDEVP(B3:B32)			D3=$B$36
36	LCL	43.68851			B35=B33+3*B34/SQRT(1)			
37					B36=B33-3*B34/SQRT(1)			



The process went out of control on Day 21.

8-27.

	A	B	C	D	E	F	G	H
1	**Pb 8-27**							
2	**Day**	**Mean**	**SD**	**$\Sigma(x_i-x_{ave})^2$**	**UCL**	**LCL**		
3	1	96.50	0.80	3.20	98.08	94.97		
4	2	97.38	0.88	3.87	98.08	94.97		
5	3	96.85	1.43	10.22	98.08	94.97		
6	4	96.64	1.59	12.64	98.08	94.97		
7	5	96.87	1.52	11.55	98.08	94.97		
8	6	95.52	1.27	8.06	98.08	94.97		
9	7	96.08	1.16	6.73	98.08	94.97		
10	8	96.48	0.79	3.12	98.08	94.97		
11	9	96.63	1.48	10.95	98.08	94.97		
12	10	95.47	1.30	8.45	98.08	94.97		
13	11	97.38	0.88	3.87	98.08	94.97		
14	12	96.85	1.43	10.22	98.08	94.97		
15	13	96.64	1.59	12.64	98.08	94.97		
16	14	96.87	1.52	11.55	98.08	94.97		
17	15	95.52	1.27	8.06	98.08	94.97		
18	16	96.08	1.16	6.73	98.08	94.97		
19	17	96.48	0.79	3.12	98.08	94.97		
20	18	96.63	1.48	10.95	98.08	94.97		
21	19	95.47	1.30	8.45	98.08	94.97		
22	20	96.43	0.75	2.81	98.08	94.97		
23	21	97.06	1.34	8.98	98.08	94.97		
24	22	98.34	1.60	12.80	98.08	94.97		
25	23	96.42	1.22	7.44	98.08	94.97		
26	24	95.99	1.18	6.96	98.08	94.97		
27								
28	Mean	96.52		**Spreadsheet Documentation**				
29	*N*	24		B28=AVERAGE(B3:B26)				D3=C3^2*5
30	s_{pooled}	1.269523		B29=COUNT(A3:A26)				E3=$B$31
31	UCL	98.07901		B30=SQRT(SUM(D3:D26)/(B29*6-B29))				F3=$B$32
32	LCL	94.96933		B31=B28+3*B30/SQRT(6)				
33				B32=B28-3*B30/SQRT(6)				



The process went out of control on Day 22.